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Four Zinc(II) Helical Coordination Polymers and 78-Membered Six-Node Zinc Metallacycle Assembled from Diastereopure *N,N′*-Bis(acetylacetone)cyclohexanediimine

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The interaction of the diastereopure *N,N′*-bis(acetylacetone)cyclohexanediimine ligands, **L**^{1}(1*R*,2*R*), **L**^{2} (1*S*,2*S*), and their 1:1 mixture, with Zn(II) chloride has been investigated. Four new coordination polymers, $[\mathrm{Zn}\mathbf{L}^1\mathrm{Cl}_2\cdot\mathrm{H_2O}]_n$ (**1**), $[\mathrm{Zn}\mathbf{L}^2\mathrm{Cl}_2\cdot\mathrm{H_2O}]_n$ (**2**), $[\mathrm{Zn}\mathbf{L}^2\mathrm{Cl}_2]_n$ (**3**), and $[\mathrm{Zn}_6(\mathbf{L}^2)_6\mathrm{Cl}_{12}\cdot 2\mathrm{H_2O}]_n$ (**4**), each consisting of an infinite single helical chain displaying different pitches and/or handedness have been isolated. The complexed Schiff base ligands are present in their deprotonated enol forms, and the nitrogen atoms, which do not coordinate, are protonated because of proton transfer from the adjacent enol oxygen (coupled with concomitant N−H···O bond formation); each bound ligand is thus pseudo-zwitterionic. The respective zinc centers are bound to two chloro ligands and two oxygen donors from acacH-imine units belonging to different *N,N′*-bis(acetylacetone)cyclohexanediimine ligands such that the coordination at each zinc is distorted tetrahedral. Compounds **1** and **2**, prepared from enantiopure **L**^{1} and **L**^{2}, respectively, are enantiomers with similar structures, with the helical pitch in each being 17.0 Å. Overall, the structure of **3** may be described as a one-dimensional helical chain with a pitch of 17.3 Å, with each period corresponding to two **L**^{2} ligands and two metal centers. The structure of $[(\mathrm{Zn}_6\mathbf{L}^2{}_6\mathrm{Cl}_{12})\cdot 2\mathrm{H_2O}]_n$ (**4**) contains six Zn(II) centers connected via six **L**^{2} ligands to form a “bowed” helical repeat unit, with the pitch of the helix corresponding to 43.5 Å. Supramolecular (intra- and intermolecular) aspects of all these unusual polymeric structures are discussed. Finally, the synthesis and characterization of an unprecedented six zinc-node discrete supramolecular assembly, $[\mathrm{Zn}_6(\mathbf{L}^1)_3(\mathbf{L}^2)_3\mathrm{Cl}_{12}]$ (**5**), incorporating a 78-membered metallacycle, is also reported.

Introduction

The design and synthesis of both discrete and extended metallo-assemblies, particularly those with interesting topologies and/or potential applications, have received very substantial attention over recent years.[1−3] In particular, interest in self-assembled coordination polymers containing one-, two-, and three-dimensional (1D, 2D, 3D) coordination arrays has grown rapidly,[4] with many of the structures falling into the realm of metal organic frameworks (MOFs). Such framework materials exhibiting luminescence/fluorescence,[5] nonlinear optical,[6] and magnetic spin-crossover[7] behavior as well as other unusual magnetic properties[8] have all been documented. Further, it has been well established that a number of porous MOF materials show very considerable promise as alternatives to zeolites in a range of applications,[9−14] including their use for gas adsorption and storage,[15] as catalysts,[16] and as ion-exchange materials.[17]

Framework materials of single handedness are a further class of metal organic arrays of considerable recent interest, driven in part by their potential use as asymmetric catalysts.[18] While the use of enantiopure ligands to introduce chirality into framework materials has now been well documented,[19] the use of chiral diamines such as *trans*-1*R*,2*R*-diaminocyclohexane for the synthesis of chiral Schiff base ligands derived from acetylacetone (acacH) has received only limited attention.[20]

We now report the results of an investigation of this type involving the interaction of the diastereopure bis(acetylac-

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Table 1. Crystallographic Data for Compounds **1**−**5**

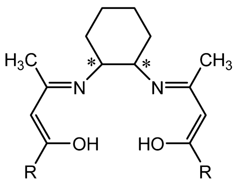
	1	**2**	**3**	**4**	**5**
empirical formula	$C_{16}H_{28}Cl_2N_2O_3Zn$	$C_{16}H_{28}Cl_2N_2O_3Zn$	$C_{16}H_{26}Cl_2N_2O_2Zn$	$C_{48}H_{80}Cl_6N_6O_7Zn_3$	$C_{96}H_{160}Cl_{12}N_{12}O_{14}Zn_6$
formula wt	432.67	432.67	414.66	1261.99	2524.22
space group	$P2_12_12_1$	$P2_12_12_1$	*Fddd*	$P2_12_12$	$R\bar{3}$
a/Å	8.904(4)	8.8874(5)	16.181(3)	15.9694(14)	24.2216(8)
b/Å	13.909(6)	13.7594(7)	17.327(3)	43.457(4)	24.2216(8)
c/Å	17.082(8)	17.0043(9)	27.663(6)	9.0848(8)	18.5242(12)
α (deg)	90.00	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00	90.00	120.00
V (Å^3)	2115.5(16)	2079.38(19)	7756(3)	6304.7(10)	9411.9(8)
Z	4	4	16	4	3
ρ_{calc} (g cm^{-3})	1.359	1.382	1.421	1.323	1.338
μ (mm^{-1})	1.428	1.453	1.552	1.433	1.440
$N_{ind}/N_{var.}$	4113/ 217	4068/222	1909/107	12188/643	4100/215
Residuals	0.0541	0.0429	0.0243	0.0517	0.0429
R1(F) (wR2(F^2))	(0.1648)	(0.1107)	(0.0698)	(0.1373)	(0.1367)
Flack parameter	0.01(3)	0.023(18)	N/A	0.002(13)	N/A
residual extrema (e Å^{-3})	0.610, −0.557	0.913, −0.641	0.326, −0.230	0.883, −0.491	0.849, −0.345

Table 2. Selected Bonds Lengths (Å) and Angles (deg) for **1**−**5**

	1		
O(1)−Zn(1)	1.989(3)	Cl(1)−Zn(1)	2.204(2)
O(2)−Zn(1)	1.984(3)	Cl(2)−Zn(1)	2.214(19)
C(2)−O(2)−Zn(1)	132.4(3)	C(15)^a−O(1)−Zn(1)	131.8(3)
	2		
O(1)−Zn(1)	1.978(2)	Cl(1)−Zn(1)	2.2215(14)
O(2)−Zn(1)	1.982(2)	Cl(2)−Zn(1)	2.1989(15)
C(2)−O(1)−Zn(1)	131.6(2)	C(10)−O(2)−Zn(1)	130.9(2)
	3		
O(1)−Zn(1)	1.9810(13)	Cl(1)−Zn(1)	2.2340(6)
C(2)−O(1)−Zn(1)	136.61(12)		
	4		
O(1)−Zn(1)	1.972(4)	O(4)−Zn(2)	1.966(4)
O(2)−Zn(1)	1.966(3)	O(5)−Zn(3)	1.983(4)
O(3)−Zn(2)	1.969(4)	O(6)−Zn(3)	1.974(4)
O(1)−Zn(1)−O(2)	108.17(15)	O(5)−Zn(3)−O(6)	107.78(17)
O(3)−Zn(2)−O(4)	107.20(17)		
	5		
O(1)−Zn(1)	1.974(3)	Cl(1)−Zn(1)	2.2552(10)
O(2)−Zn(1)	1.987(3)	Cl(2)−Zn(1)	2.2005(11)
C(4)−O(1)−Zn(1)	139.3(3)	C(7)−O(2)−Zn(1)	139.3(3)
O(1)−Zn(1)−O(2)	102.81(11)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 3/2, -y, z - 1/2$.

etone)cyclohexanediimine ligands **L^1** (1*R*,2*R*) and **L^2** (1*S*,2*S*) with Zn(II). This d^{10} metal ion is free of crystal field steric dictates and thus allows maximum coordination shell flexibility in forming metallo species, a well utilized strategy in the past for this metal.[21]



L^1 = (1R,2R)
L^2 = (1S,2S)

Experimental Section

Materials and General Methods. All reagents employed for syntheses were obtained commercially and used either as supplied or purified by standard methods prior to use. Elemental (C, H, N) analysis data were obtained with a Vario ELIII elemental analyzer. IR spectra were recorded using KBr pellets on a Bio-Rad FTIR spectrophotometer (in the 400−4000 cm^{-1} range).

Syntheses of 1*R*,2*R*- and 1*S*,2*S*-Bis(acetylacetone)cyclohexanediimine Ligands (L^{1}and L^2). The syntheses of **L^1** and **L^2** were based on literature precedence.[22,23] For **L^1**, yield, 58%. Anal. Calcd (%) for $C_{16}H_{26}O_2N_2$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.18; H, 9.35; N, 10.09. IR (KBr pellet/cm^{-1}): 3069(w), 2940(s), 2857(m), 1612(s), 1512(s), 1442(m), 1357(m), 1304(s), 1124(m), 1022(w), 994(w), 814(m), 744(m). For **L^2**, yield, 65%. Anal. Calcd (%) for $C_{16}H_{26}O_2N_2$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.08; H, 9.37; N, 10.12. IR (KBr pellet/cm^{-1}): 3068(w), 2940(s), 2855(m), 1612(s), 1513(s), 1441(m), 1355(m), 1304(s), 1123(m), 1022(w), 995(w), 814(m), 745(m).

Synthesis of (ZnL^{1}Cl$_2$·H$_2$O)$_n$ (1). $ZnCl_2 \cdot 2H_2O$ (140 mg, 1 mmol) in ethanol (10 mL) was added dropwise with stirring to **L^1** (278 mg, 1.00 mmol) in ethanol (30 mL) and stirring was continued at room temperature for 5 h. The precipitate that formed was collected by filtration, washed with ethanol, and dried at room temperature to give **1** as a white solid in 42% yield. The solid was dissolved in excess ethanol at room temperature; slow evaporation of this solution yielded colorless block-shaped single crystals that proved suitable for X-ray analysis. The crystals were filtered off and dried in air. Calculated for $C_{16}H_{26}Cl_2N_2O_2Zn \cdot H_2O$: C, 44.41; H, 6.52; N, 6.47; found: C, 44.36; H, 6.48; N, 6.52. IR (KBr pellet/cm^{-1}): 3557(m), 3489(w), 3070(w), 2940(w), 2860(w), 1606(m), 1551(s), 1437(w), 1339(m), 1256(w), 1212(w), 1115(w), 1015(w), 951(m), 796(w), 475(w), 448(w).

Synthesis of [ZnL^{2}Cl$_2$·H$_2$O]$_n$ (2). Compound **2** was prepared from $ZnCl_2 \cdot 2H_2O$ and **L^2** in 46% yield via an analogous procedure to that employed for [ZnL^{1}Cl$_2$·H$_2$O]$_n$ (**1**). Colorless single crystals suitable for X-ray analysis were obtained on slow recrystallization of the product from ethanol. Calcd (%) for $C_{16}H_{26}Cl_2N_2O_2Zn \cdot H_2O$: C, 44.41; H, 6.52; N, 6.47; found: C, 44.33; H, 6.57; N, 6.53. IR

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Table 3. Formal Hydrogen Bonding Geometries for **1**−**5**

donor	acceptor	D−H (Å)	H−A (Å)	D−A (Å)	DHA angle (deg)
			1		
N(1)−H(1)	O(1)[a]	0.86	1.98	2.676(4)	136.7
N(2)−H(2)	O(2)	0.86	1.94	2.643(4)	137.9
			2		
N(1)−H(1)	O(1)	0.86	1.93	2.632(3)	137.7
N(2)−H(2)	O(2)	0.86	1.99	2.672(3)	135.9
			3		
N(1)−H(1)	O(1)	0.86	1.97	2.665(2)	137.3
			4		
N(1)−H(1)	O(1)	0.86	1.99	2.684(5)	136.4
N(2)−H(2)	O(2)	0.86	1.93	2.623(5)	136.9
N(3)−H(3A)	O(3)	0.86	1.91	2.608(5)	137.7
N(4)−H(4)	O(4)	0.86	1.97	2.661(5)	136.5
N(5)−H(5)	O(5)	0.86	1.92	2.614(5)	137.2
N(6)−H(6A)	O(6)	0.86	1.93	2.624(5)	136.5
			5		
N(1)−H(1)	O(1)	0.86	1.93	2.637(4)	138.6
N(2)−H(2)	O(2)	0.86	1.98	2.657(4)	134.3

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1/2$, $-y$, $z + 1/2$.

(KBr pellet/cm^{-1}): 3555(m), 3487(w), 3071(w), 2940(w), 2860(w), 1608(m), 1550(s), 1438(w), 1336(m), 1256(w), 1213(w), 1115(w), 1016(w), 952(m), 796(w), 477(w), 2446(w).

Synthesis of [ZnL^{2}Cl$_2$]$_n$ (3). A mixture of $ZnCl_2\cdot 2H_2O$ (140 mg, 1 mmol) and **L^2** (278 mg, 1.00 mmol) in ethanol (20 mL) was stirred at room temperature for 1 h. Molecular sieves (4 Å, 50 mg) were added to the resulting clear solution. After 12 h the molecular sieves were filtered off and the filtrate was allowed to evaporate to give colorless crystals that proved suitable for X-ray analysis. The remainder of the crystalline product was dried under vacuum before analysis. Yield, 12%. Anal. Calcd (%) for $C_{16}H_{26}Cl_2N_2O_2$ Zn: C, 46.34; H, 6.32; N, 6.76. Found: C, 46.31; H, 6.30; N, 6.71. IR (KBr pellet/cm^{-1}): 3071(w), 2941(w), 2859(w), 1608(m), 1551(s), 1438(w), 1338(m), 1256(w), 1215(w), 1113(w), 1016(w), 951(m), 797(w), 474(w), 445(w).

Synthesis of [(Zn$_6$(L^2)$_6$Cl$_{12}$)·H$_2$O]$_n$ (4). $ZnCl_2\cdot 2H_2O$(140 mg, 1 mmol) and imidazole (68 mg, 1.0 mmol) was added slowly to **L^2** (278 mg, 1.00 mmol) in ethanol (20 mL). The mixture was stirred for 1 h, and the initial white precipitate that formed was filtered off. The filtrate was allowed to evaporate slowly to yield colorless single crystals that proved suitable for X-ray analysis. The remainder of this crystalline product was washed with ethanol and dried under vacuum before analysis. Yield, 42%. Anal. Calcd (%) for $C_{96}H_{156}Cl_{12}N_{12}O_{12}Zn_6\cdot H_2O$: C, 46.01; H, 6.35; N, 6.71. Found: C, 46.84; H, 6.36; N, 6.86. IR (KBr pellet/cm^{-1}): 3500(m), 3070(w), 2944(w), 2859(w), 1610(m), 1551(s), 1437(w), 1336(m), 1258(w), 1213(w), 1116(w), 1015(w), 952(m), 795(w), 478(w), 446(w).

Synthesis of Zn$_6$(L^1)$_3$(L^2)$_3$Cl$_{12}$·H$_2$O (5). $ZnCl_2\cdot 2H_2O$ (140 mg, 1 mmol) in ethanol (10 mL) was slowly added to a stirred solution of **L^1** (278 mg, 1.00 mmol) and **L^2** (278 mg, 1.00 mmol) in ethanol (30 mL). Stirring was continued for 30 min, and the white precipitate that formed was collected by filtration, washed with ethanol, and dried under vacuum before analysis. Yield: 56%. Block-shaped single crystals suitable for X-ray analysis were obtained by recrystallization of this product from ethanol. Anal. Calcd (%) for $C_{96}H_{156}Cl_{12}N_{12}O_{12}Zn_6.H_2O$: C, 46.01; H, 6.35; N, 6.71. Found: C, 46.26; H, 6.31; N, 6.71. IR (KBr pellet/cm^{-1}): 3561(s), 3215(m), 3112(w), 2859(w), 1610(s), 1551(s), 1442(w), 1376(m), 1341(m), 1252(w), 1210(w), 1125(w), 1032(w), 948(w), 859(w), 793(w), 763(w), 713(w), 524(w), 453(w).

X-ray Data Collection and Structure Determinations. Single crystal X-ray diffraction studies of **1**−**5** were performed at room temperature on a Bruker Smart Apex single crystal diffractometer using the φ-ω scan method. The data were collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements, and multiscan absorption corrections were applied using the SADABS program. All of the structures were solved by direct methods using the program SHELXS86 in the winGX package[24] Crystallographic data are summarized in Table 1, and the elected bond lengths and angles are given in Table 2, respectively.

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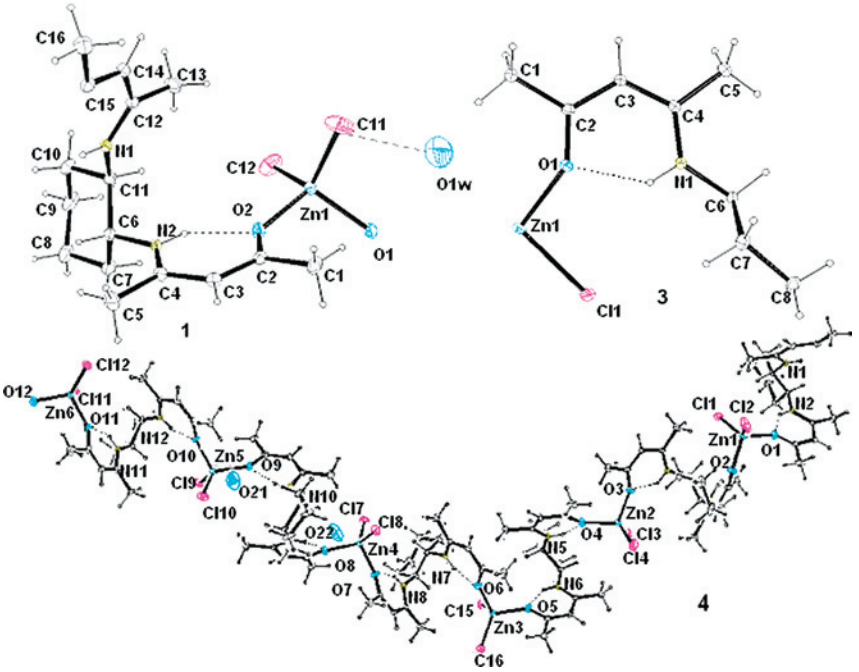

Figure 1. ORTEP representations of **1**, **3**, and **4** showing atom numbering schemes and 10% thermal ellipsoids; the structure of **2** is similar to **1** but of opposite handedness. Dashed lines indicate intramolecular ionic $N^{+}-H\cdots O^{-}$ hydrogen bonds. Water solvate molecules are not shown.

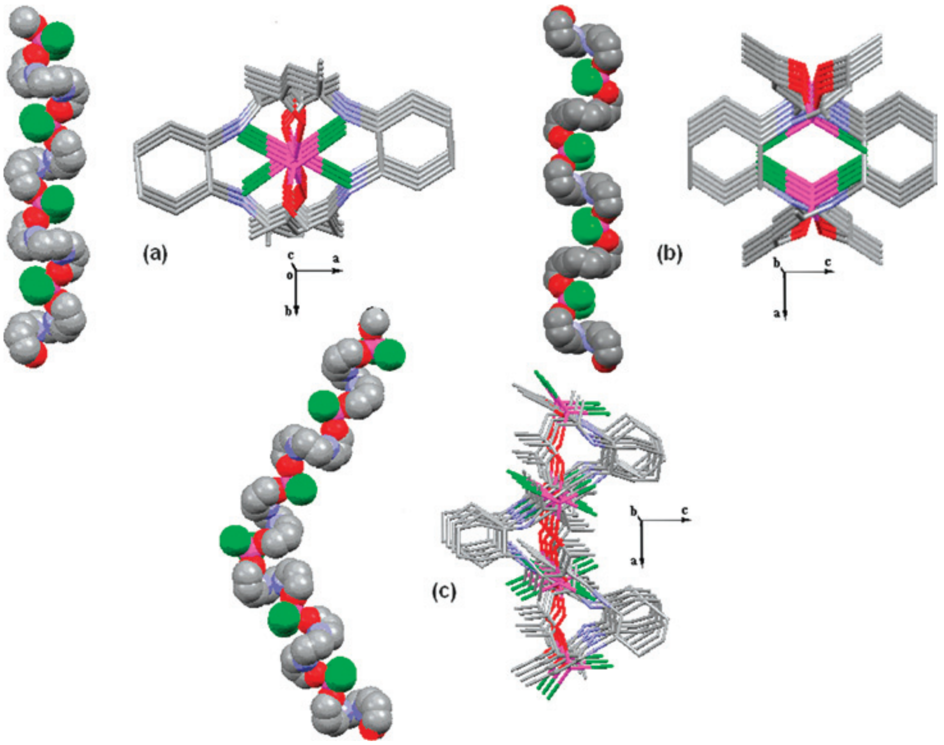

Figure 2. (a) 1D helical chain in $[(Zn\mathbf{L}^1Cl_2)\cdot H_2O]_n$ (**1**) viewed along the crystallographic *a* axis and top view from slightly off the *c* axis. (b) The 1D helical chain in $[Zn\mathbf{L}^2Cl_2]_n$ (**3**) viewed along the crystallographic *c* axis and top view from slightly off the *b* axis. (c) The 1D right-handed helical chain in $[Zn_6(\mathbf{L}^2)_6Cl_{12}\cdot 2H_2O]_n$ (**4**) showing the repeat unit incorporating six zinc centers viewed along the crystallographic *c* axis and top view from slightly off the *b* axis. Hydrogen atoms, methyl groups attached to acetylacetone fragments, and water molecules are omitted for clarity. C, gray; Cl, green; Zn, pink; O, red; and N, blue.

Results and Discussion

Synthesis of Zn(II) Derivatives of $\mathbf{L}^1$ and $\mathbf{L}^2$. $[(Zn\mathbf{L}^1Cl_2)\cdot H_2O]_n$ (**1**), $[(Zn\mathbf{L}^2Cl_2)\cdot H_2O]_n$ (**2**), $[Zn\mathbf{L}^2Cl_2]_n$ (**3**), $[(Zn_6\mathbf{L}^2{}_6Cl_{12})\cdot 2H_2O]_n$ (**4**), and $[(Zn_6(\mathbf{L}^1)_3(\mathbf{L}^2)_3Cl_{12})\cdot H_2O]$ (**5**) were isolated as colorless air-stable crystals by reaction of $\mathbf{L}^1$ and/or $\mathbf{L}^2$ with $ZnCl_2\cdot 2H_2O$ in ethanol under defined conditions; each product exhibits a similar 1:1 ratio of $ZnCl_2$ to **L**. While similar conditions were employed for the synthesis and isolation of the enantiomeric assemblies **1** and **2** (starting from $\mathbf{L}^1$ or $\mathbf{L}^2$ respectively), **3** and **4** were isolated

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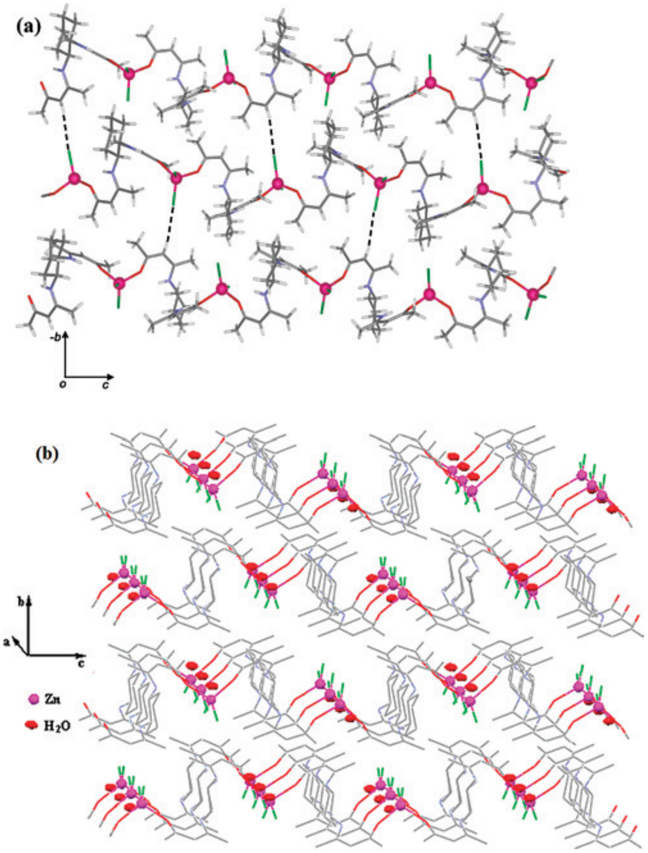

Figure 3. (a) 2D network in $[(\mathrm{Zn}\mathbf{L}^1\mathrm{Cl}_2)\cdot\mathrm{H_2O}]_n$ (**1**) involving the C(14)−H(14)···Cl(2)$^{\mathrm{i}}$ (i = 1/2 + x, −1/2 − y, −z) hydrogen bonds. Water molecules have been omitted for clarity. The intermolecular C_γ−H···Cl hydrogen bonds are shown as dashed lines. (b) The wave-like structure of **1** viewed slightly obliquely to the *a* axis. Hydrogen atoms have been omitted for clarity. Other weak C−H···Cl interactions (not shown) are present between the layers.

under other conditions. Both **1** and **2** were obtained as monohydrates (with respect to each monomeric unit) while, in the case of **3**, the synthesis was performed in the presence of molecular sieves to yield an anhydrous product. For **4**, a related procedure was again employed except that 1 equiv of imidazole was present in the reaction solution. The preparation of **5** involved a similar procedure to that used for **1** and **2** except that an equimolar mixture of $\mathbf{L}^1$ and $\mathbf{L}^2$ was employed for the reaction.

Crystal Structures of the Zn(II) Derivatives. Details of the X-ray structures of **1**−**4** are given in Figures 1−5 and Tables 1−3; the asymmetric units for **1**−**2** each contain one zinc atom and one Schiff base ligand, that for **3** contains half of one zinc ion and half of one ligand, while that for **4** contains three zinc atoms and three ligands. All four compounds show some common structural features. The respective zinc centers are each bound to two chloro ligands and two oxygen donors from acacH-imine units belonging to different *N,N′*-bis(acetylacetone)cyclohexanediimine ligands of type $\mathbf{L}^1$ or $\mathbf{L}^2$, and the coordination environment around zinc is best described as distorted tetrahedral in each case; all Zn−O and Zn−Cl bond lengths (Table 2) are unremarkable. The complexed Schiff base ligands are present in their deprotonated enol forms, and the nitrogen atoms, which do not coordinate, are protonated because of proton transfer from the adjacent enol oxygen. An intramolecular ionic $\mathrm{N^+}$−H···$\mathrm{O^-}$ hydrogen bond (Table 3) links each nitrogen

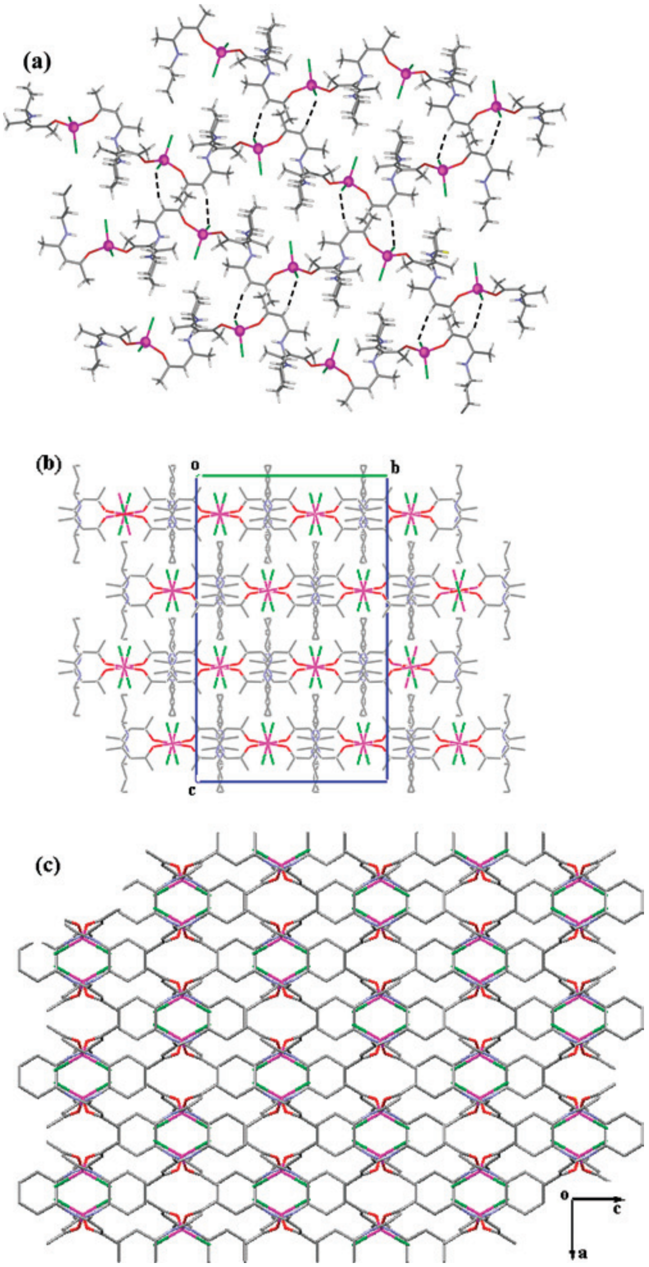

Figure 4. (a) View of $[\mathrm{Zn}\mathbf{L}^2\mathrm{Cl}_2]_n$ (**3**) showing C−H···Cl hydrogen bonds connecting helical chains as dashed lines.(b) View of the quasi 2D chiral layers of **3** that extend parallel to the crystallographic *bc* plane. (c) The non-interpenetrating framework of **3** viewed down the crystallographic *b* axis. Hydrogen atoms are not shown.

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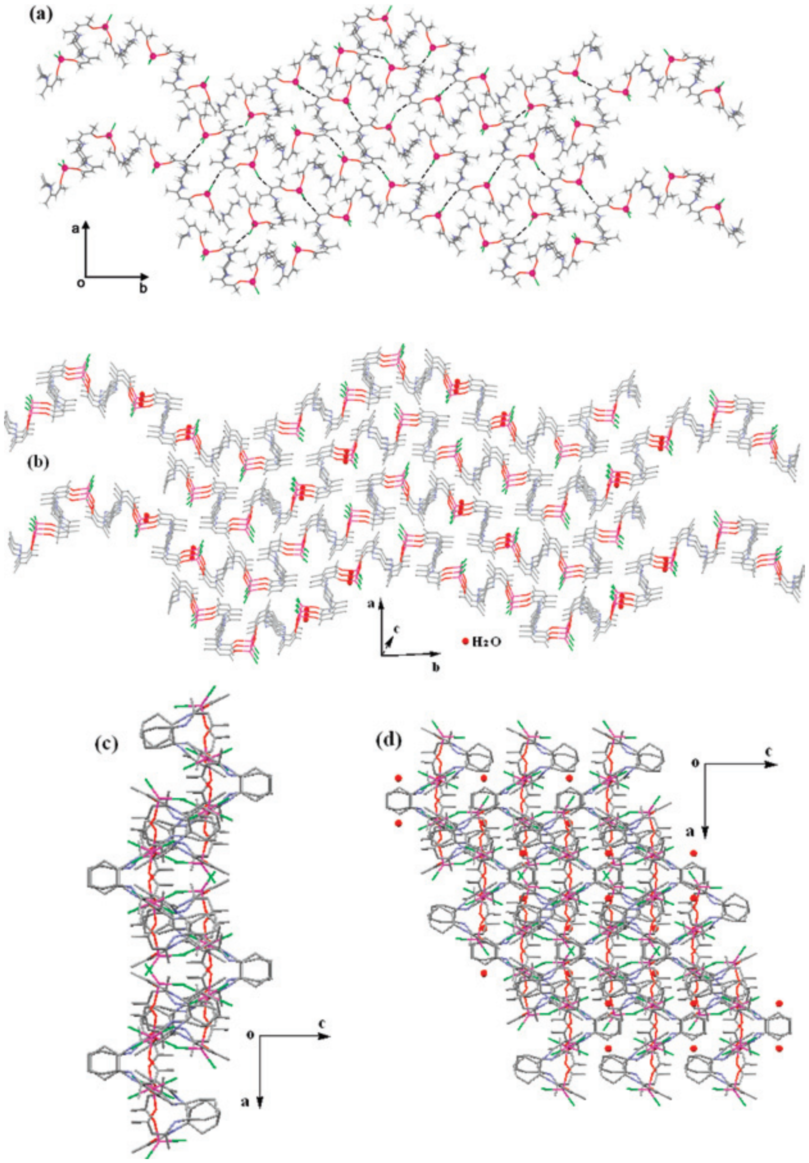

Figure 5. (a) View of $[(Zn_6\mathbf{L^2}_6Cl_{12})\cdot 2H_2O]_n$ (**4**) showing the 2D network. The C−H···Cl hydrogen bonds connecting adjacent chains are shown as dashed lines. (b) View of how the chiral chains in **4** are extended along the crystallographic *c*-axis to form the wave-like arrangement. (c) Part of the quasi 3D network viewed down the crystallographic *b* axis. (d) The quasi 3D network viewed down the crystallographic *b* axis showing the location of the water molecules. Hydrogen atoms are not shown.

atom to the corresponding nearby terminal oxygen atom of the same ligand such that a coplanar six-membered ring (incorporating the hydrogen bond) is generated (see Figure 1). This results in each bound acacH-imine domain having pseudo-zwitterionic character. X-ray analyses confirm that **1** and **2**, prepared from enantiopure $\mathbf{L^1}$ and $\mathbf{L^2}$ repectively, are enantiomers with otherwise similar structures (see below) while **2**−**4** may be classified as polymorphic or pseudo-polymorphic with respect to each other.

In **1** and **2**, each Schiff base ligand bridges between Zn(II) centers via its terminal oxygen atoms to form single-stranded helical chains oriented along the crystallographic *a* axis. For each 1D chain the axis of the helix passes through successive Zn(II) centers; that is, when viewed from the top of the chain, the Zn(II) ions are located along the helical axis (shown for **1** in Figure 2a). Reflecting the "opposing" arrangement of the $C-N_{imine}$ bonds in the rigid *trans*-1,2-cyclohexyl moiety, these polymeric chains in **1** and **2** display *M* and *P* handedness, respectively. The mean X-ray determined period of the helix in each is 17.0 Å; as expected, the experimental values for the other corresponding distances and angles in these enantiomeric compounds (see Table 2) do not deviate significantly from the respective mean X-ray values. The dihedral angles between the two coplanar six-membered (hydrogen-bonded) rings (Table 3) on the acacH-imine "arms" of the same ligand ($\mathbf{L^1}$ or $\mathbf{L^2}$) are 113° for **1** and **2**, while a value of 93° was obtained for the angles between the corresponding six-membered ring planes on adjacent ligands bound to Zn(II). The Cl−Zn−Cl angle in each complex is 117°. The asymmetric units for **1** and **2** each contain a water molecule that is weakly hydrogen bonded to a chloro ligand (indicated by O−Cl distances of ~3.01 Å, noting that the O-bound hydrogen atoms were not modeled).

The individual 1D left- and right-handed helical chains in **1** and **2** are in each case linked in a similar manner to

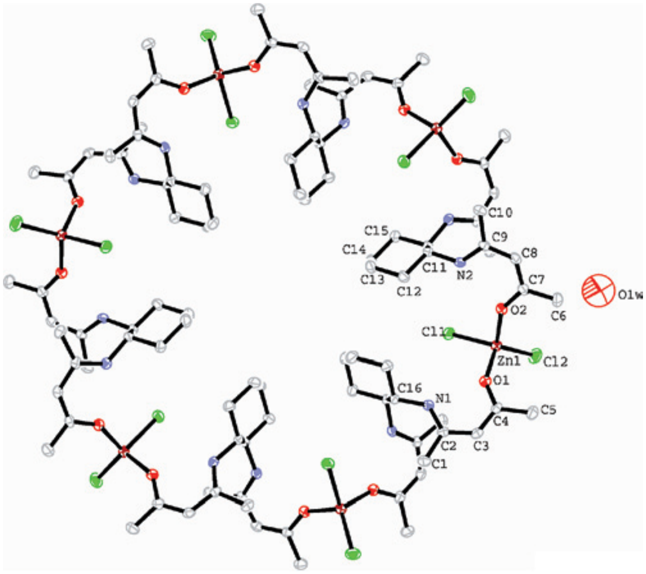

Figure 6. Structure of the 78-membered metallacyclic ring in $[Zn_6(\mathbf{L^1})_3(\mathbf{L^2})_3Cl_{12}\cdot H_2O]$ (**5**), viewed along the *c*-direction. Ellipsoids are drawn with 30% probability. C, gray; Cl, green; Zn, pink; O, red; N, blue.

adjacent chains in the lattice via $C_\gamma-H\cdots Cl$ hydrogen bonds ($H(13)-Cl(2) \sim 3.06$ Å in **1**) to form 2D layer arrays (shown for **1** in Figure 3a,b); in both these compounds the 2D chiral layers propagate in the crystallographic *bc* plane. Other hydrogen bonding interactions are also present between the above layers; if these are taken into account then **1** and **2** can be considered to adopt a quasi 3D arrangement. The shortest Zn···Zn distance between adjacent chains is 8.9Å.

In $[Zn\mathbf{L^2}Cl_2]_n$ (**3**), the terminal oxygen atoms of the two acacH-imine units of each $\mathbf{L^2}$ also link zinc centers to form single-strand chains displaying right-handed helicity along the crystallographic *b* axis (Figure 2b). The O−Zn−O bond angle is 124°, the dihedral angle between the two six-numbered rings formed from each hydrogen bonded acacH-imine "arm" of the same $\mathbf{L^2}$ ligand is 126°, while that between the corresponding two six-membered ring planes (incorporating a hydrogen bond) on the different ligands bound to a Zn(II) is ~122°. Overall, the structure of **3** may be described as a helical 1D chain with a pitch of 17.3 Å, with each period corresponding to two $\mathbf{L^2}$ ligands and two zinc centers. The 1D helical chains are interconnected by $C_\gamma-H\cdots Cl$ hydrogen bonds ($H(3)-Cl(1) \sim 3.06$ Å) between adjacent chains to form quasi 2D layers (Figure 4a), the layers extended parallel to the crystallographic *bc* plane (Figures 4b), with the shortest Zn···Zn distance between chains being 5.1 Å. Viewed along the crystallographic *a* axis, they are seen to form a non-interpenetrating framework (Figure 4c).

In $[(Zn_6\mathbf{L^2}_6Cl_{12})\cdot 2H_2O]_n$ (**4**) six Zn(II) centers are connected via six $\mathbf{L^2}$ ligands to form a "bowed" structural repeat unit, with the metal−metal separation varying from 8.4 to 8.9 Å (Figure 2c). This corresponds to a pitch of 43.5 Å. When viewed from the top of the chain, the Zn(II) atoms are located in four lines along the crystallographic *c* axis (Figure 2c). The terminal oxygen atoms of the two acacH-imine units of each $\mathbf{L^2}$ again link zinc centers to form single-strand chains displaying left-handed helicity along the crystallographic *b* axis. There are several O−Zn−O bond angles present, ranging from 107.2 to 108.2°, while the dihedral angles between the hydrogen bond-containing (Table 3) six-membered rings involving the acacH-imine "arms" of the same $\mathbf{L^2}$ vary from 115 to119°. The angles between the two six-numbered hydrogen bond-ring planes linked to the same Zn(II) range from 94 to 97°. Adjacent 1D helical chains in **4** are interconnected by intermolecular $C_\gamma-H\cdots Cl$ hydrogen bonds ($H(27)-Cl(2) \sim 2.88$ Å) to form a 2D framework along the crystallographic *a* axis (see Figure 5a). These 2D chiral layers are extended along the crystallographic *c* axis to give the wavelike structure shown in Figure 5b, and the structure also contains two hydrogen bonded water molecules linked to the two chloride ligands, respectively (indicated by an O(1w)−Cl(2) separation of ~3.09Å, noting that the O-bound hydrogen atoms were not modeled). When viewed along the crystallographic *b* axis, the 2D frameworks are extended into quasi 3D structures (Figures 5c and 5d). The shortest Zn···Zn distance between adjacent layers in the wavelike structure is 9.1 Å.

The metallacyclic structure of $Zn_6(\mathbf{L^1})_3(\mathbf{L^2})_3Cl_{12}\cdot H_2O$ (**5**), which crystallizes in the trigonal $R\bar{3}$ space group, is shown in Figure 6. Six zinc ions and six bridging ligands (namely three $\mathbf{L^1}$ and three $\mathbf{L^2}$, alternatively ordered) combine to form a highly unusual S_6 symmetric 78-membered metallacyclic ring. The pseudo-tetrahedral Zn(II) ions are each bound to two terminal enolate-O atoms from $\mathbf{L^1}$ and $\mathbf{L^2}$ ligands, as well as to two chloro ligands (see Figure 7); the Zn−Cl bond lengths are

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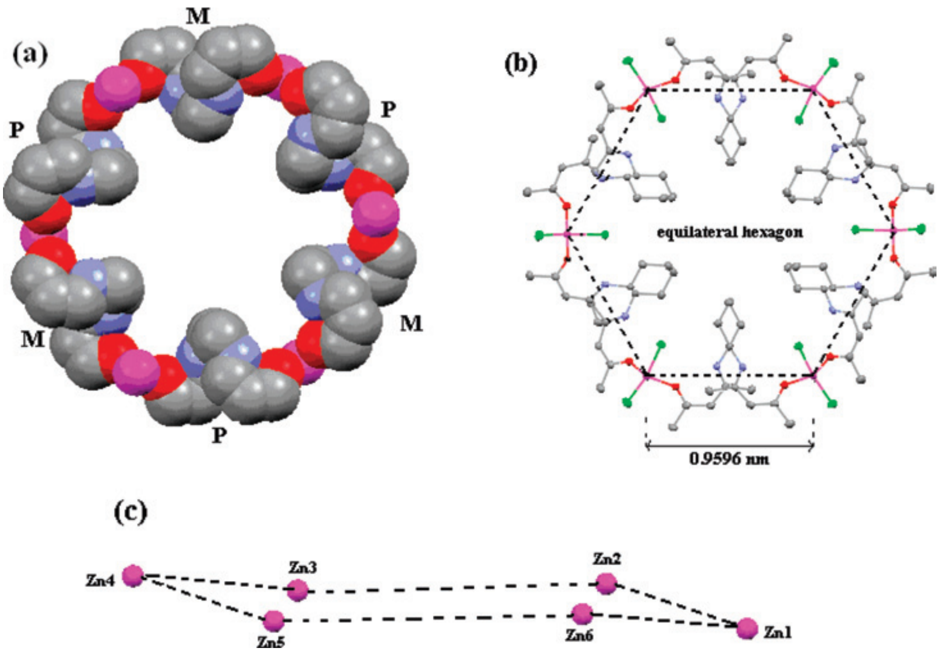

Figure 7. (a) Space filling model of $Zn_6(\mathbf{L^1})_3(\mathbf{L^2})_3Cl_{12}\cdot H_2O$ (**5**) showing the reciprocal helical path composed of *M* and *P* handed units; hydrogen atoms, chloro ligands, and water molecule not shown. (b) The hexagonal structure of **5** viewed down the *c*-axis. (c) The chair arrangement defined by the six zinc centers in individual metallacyclic rings. C, gray; Cl, green; Zn, pink; O, red; N, blue.

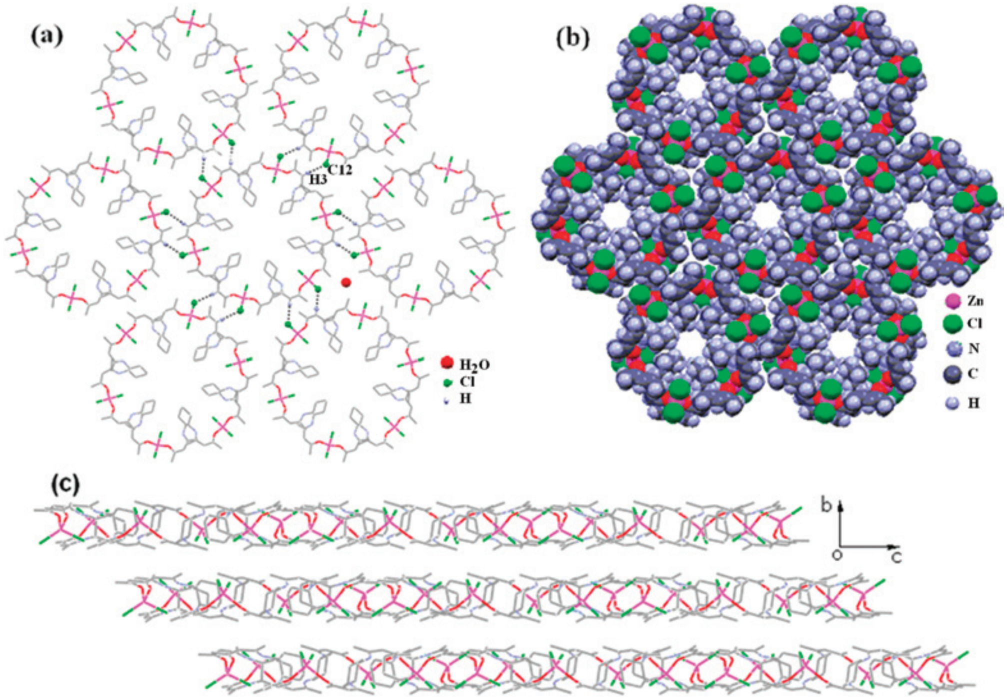

Figure 8. (a) View of the quasi 2D network in $Zn_6(\mathbf{L^1})_3(\mathbf{L^2})_3Cl_{12}\cdot H_2O$ (**5**), showing the network of hydrogen bonds (C(3)−H···Cl(2)^v, v = $-x$, $1/2 + y$, $1/2 - z$) linking metallacycles (shown as dashed lines). (b) Space-filling diagram of the 2D semiporous network viewed down the *c*-axis. (c) The layered structure of **5**; the water molecules (not shown) are located in the interlayer voids. C, gray; Cl, green; Zn, pink; O, red; N, blue.

non-equivalent at 2.255(1) and 2.200(1) Å. The O−Zn−O bond angle is 102.85°, with Zn−O bond distances of 1.975(3) and 1.986(3) Å. The dihedral angle between the two six-membered rings of the acacH-imine units bound to Zn(II) is ~140°.

The $Zn(\mathbf{L^1})(\mathbf{L^2})Cl_2$ units in **5** adopt reciprocal *M* and *P* handedness around the 78-membered metallacycle (Figure 7a). When viewed down the *c*-axis, the six Zn(II) atoms ascribe an equilateral hexagon with the adjacent Zn···Zn distance being 9.60 Å (Figure 7b). The six zinc centers defining the ring are not coplanar but define a chair arrangement (Figure 7c), with Zn(1) and Zn(4) lying respectively 1.03 Å above and below the plane formed by Zn(2), Zn(3), Zn(5), and Zn(6). The cyclohexane rings of the 1,2-diaminecyclohexane groups are orientated toward the center of the metallacyclic ring, with the latter lying in the crystallographic *ab* plane.

As indicated in Figure 8a, each metallacyclic ring is linked via Cγ−H···Cl hydrogen bonds (H(3)−Cl(2) ~ 2.91 Å) to six other such rings to yield a 2D semiporous layer structure (Figure 8b). These 2D chiral layers are arranged orthogonal to the crystallographic *bc* plane; weak intermolecular interactions occur between layers to form the layered arrangement shown in Figure 8c, with the uncoordinated water molecules situated in the interlayer voids.

Conclusion

The metal-directed interaction of diastereopure $\mathbf{L}^1$ and $\mathbf{L}^2$ with zinc chloride has resulted in the isolation and characterization of four new helical coordination polymers of type $[\mathrm{Zn}\mathbf{L}^1\mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}]_n$ (**1**), $[\mathrm{Zn}\mathbf{L}^2\mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}]_n$ (**2**), $[\mathrm{Zn}\mathbf{L}^2\mathrm{Cl}_2]_n$ (**3**), and $[\mathrm{Zn}_6(\mathbf{L}^2)_6\mathrm{Cl}_{12}\cdot 2\mathrm{H}_2\mathrm{O}]_n$ (**4**) while reaction with a mixture of these ligand isomers has resulted in generation of a unique discrete assembly of type $[\mathrm{Zn}_6(\mathbf{L}^1)_3(\mathbf{L}^2)_3\mathrm{Cl}_{12}]$ (**5**). These products are unusual on at least three counts. First, each incorporates the bound Schiff base ligand in an uncommon *neutral* (pseudo-zwitterionic) form. Second, for **1**−**4**, the extended chain structures each adopt interesting single helical configurations of different pitches and/or handedness, demonstrating that the use of individual ligand diastereomers of the present type readily leads to a family of less common metallo-supramolecular products whose helical structures clearly reflect the inherent chiral properties of the diastereopure 1,2-diaminocyclohexane backbone present in each ligand isomer. Finally, the above infinite linear arrangements adopted in **1**−**4** contrast with the discrete cyclic structure of the product that spontaneously forms when zinc chloride reacts with a mixture of $\mathbf{L}^1$ and $\mathbf{L}^2$. In this case an unprecedented 78-membered metallacycle (**5**), incorporating six zinc nodes, is generated.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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